CHAPTER II
LITERATURE REVIEWS

The selective catalytic reduction (SCR) of NO_x by ammonia has been the most widely adopted process for flue gas cleaning from stationary emissions (*e.g.* power plants), despite the recent interests for alternative types of nitric oxide removal processes. The most commonly used catalysts are vanadia/titania type materials. The reviews in this chapter will concentrate on those used in elimination NO_x from flue gas.

2.1 Reviews paper

In this section, the relevant SCR of NO_x with ammonia by V_2O_5/TiO_2 papers are summarized to raise the problem issue. They are as follows:

Morikawa *et al.* (1981) explored the retardation of the SO_2 oxidation over the V_2O_5/TiO_2 catalyst improved by the addition of a third component. In conclusion, the addition of relatively a small amount of GeO_2 to V_2O_5/TiO_2 lowered the oxidation efficiency of SO_2 to SO_3 and also raised the NO_x reduction efficiency of the parent V_2O_5/TiO_2 catalyst.

Murakami *et al.* (1983) studied the effect of supported vanadium oxides prepared by both the conventional impregnation and vapor-phase-supporting methods. TiO_2 (anatase), TiO_2 (rutile), TiO_2 (mixture of anatase with rutile), Al_2O_3, ZrO_3, SiO_2, and MgO were used as supports. It was found that the structure of the vapor-phase-supporting catalyst does not change significantly from that of the catalyst prepared by the conventional impregnation method. Also, the structure of the V_2O_5/TiO_2 catalyst does not change significantly with modification of TiO_2, *i.e.* anatase, rutile and mixture of anatase with rutile. This means that the difference in the modification of TiO_2 is too small to affect the structure of V_2O_5 on the support. On the other hand, the structure of supported vanadium oxide catalyst is greatly changed with the kinds

of support (*e.g.* TiO_2, Al_2O_3, ZrO_3, SiO_2, and MgO). These results lead to a conclusion that the structure of supported vanadium oxide is mainly determined by the kind of support, while neither the method of preparation nor the modification of support affects the structure significantly.

Shikada & Fujimoto (1983) identified the effect of added alkali salts on the activities of supported vanadium oxide catalysts for nitric oxide reduction with ammonia. They claimed that the activities of supported vanadium oxide catalysts for nitric oxide reduction were promoted by the addition of sodium or lithium salts. Conversely, the activity of supported vanadium oxide catalysts for nitric oxide reduction was suppressed by the addition of potassium salts. But the reason why the activity changes with the addition of alkali is not clear.

Okazaki *et al.* (1985) clarified the effect of Nb_2O_5 addition on the catalytic activity of iron oxide for the denitration. It was found that the activity of FeO_x catalyst containing a small amount of Nb_2O_5 could attain 90-100 % in NO conversion. In contrast, the NO conversion is less than 40 % for the reduction catalyzed by FeO_x without Nb_2O_5. The micro particles of Nb_2O_5 might be formed on FeO_x particles, and might prevent the aggregation and crystallization of iron oxide particles.

Kotter *et al.* (1989) investigated structure, selectivity and activity changes in vanadia/titania SCR catalysts that occured on heating to lower temperatures than those required to initiate the anatase-rutile transformation. Heat treatment of vanadia/titania (anatase) catalysts at temperature lower than those required for anatase-rutile transformation has been found to cause changes in the structure of the catalyst and the selectivity for the reaction between ammonia and nitric oxide. As the treatment temperature increased from 350 to $440^\circ C$, and as the time of heat treatment increased, the surface area decreased, the amount of vanadia (V) species weakly interacting with titania increased and needle-like crystals were formed. At the same time, the reduction of nitric oxide to nitrogen decreased while formation of nitrous oxide was promoted. Washing the catalyst with ammonia solution removed the crystal deposited and could avoid the production of nitrous oxide.

Centi *et al.* (1991) studied vanadium oxide supported on a TiO_2 - Al_2O_3 mixed oxide prepared by gel-supported precipitation in the presence and absence of SO_2 for the selective removal of NO_x with ammonia. The results showed that the DeNO$_x$ activity of this sample was higher in the presence of SO_2 than without. This catalyst showed enhanced properties of resistance to deactivate by SO_2 during the selective removal of NO_x with ammonia in flue gases owing to the transfer of sulphate groups to Al sites. Sulphate groups on alumina increased the strength of Brønsted acid sites owing to inductive effects. The same effect is probable also present in the V-TiO_2-Al_2O_3 system.

Tokarz *et al.* (1991) determined the effect of the emissions from burning wastes, *i.e.* from municipal waste incinerators, on the SCR- type catalyst. It was concluded that the flue gases from municipal waste incinerator contained at least 10 elements which in different ways influenced the life-time and activity of the de-NO_x catalyst. These elements were added to the catalyst in amounts corresponding to the level of 3 wt.% and used to test the reaction. Mg, K and Na showed the highest negative effect on the catalyst. Next, Fe, Al, Ca and Zn showed a moderate effect, whereas Ni, Ba and Cr showed little or no negative effect. When Mg, K and Na were added to the catalysts, NO conversion decreased. This phenomenon can probably be explained by the fact that Mg, K and Na react with V_2O_5 which is present on the surface of the catalyst, and cause the sintering which in turn may result in the disappearance of the smallest pores. Further testing of catalyst samples in a stream of flue gases for periods longer than 2,000 hours was suggested to confirm the results obtained for artificially aged catalyst samples.

Lintz & Turek (1992) investigated intrinsic kinetics of nitric oxide reduction by ammonia on a vanadia/titania catalyst. In conclusion, the reduction of nitric oxide by ammonia in the presence of oxygen can be described by the use of three linearly independent stoichiometric equations, including nitrous oxide formation and ammonia combustion. The addition of water in flue gas slightly reduced the catalyst activity but caused decisive increase of the selectivity. On the other hand the possible side reactions, the oxidation of ammonia and the formation of nitrous oxide were largely

suppressed by the presence of water. The investigation of transport phenomena has showed that strong influence of internal mass transfer resistance was expected in catalysts of technically relevant dimensions. The intrinsic kinetics can be quantified by use of a Langmuir-Hinshelwood type rate equation.

Ozkan et al. (1992) focussed on the structural specificity of vanadia catalysts in relation to their activity in selective catalytic reduction of nitric oxide and in oxidation of ammonia. The investigation of the structural of vanadia catalysts indicated that the basal plane (010) promoted the formation of N_2O and NO whereas the side plane contributed to the formation of N_2.

Lietti et al. (1993) investigated the effect of K-doping on the surface structure and catalytic properties of sub-monolayer vanadia/titania de-NO_xing catalysts. It was exhibited that the nature of the surface vanadium oxide species in wet condition did not change significantly upon K doping. However, the stretching frequencies of surface vanadyls of K doping catalysts were lower for undoped catalysts due to the production of strong oxide basic anions on the catalyst surface that act as ligands for the vanadyl complexes. This reduces the Lewis acidity of vanadium ions. IR and TPD (Temperature Programmed Desorption) experiments indicated that both molecularly chemisorbed ammonia and ammonium ions were present in much lower amounts and were less strongly held on K-doped samples. TPD and TPSR (Temperature Programmed Surface Reaction) data further indicated that the alkali dopant poisoned preferentially Lewis acid sites associated with vanadium rather than with Ti^{4+} ions. Also, TPSR and TPR data showed that alkali doping reduced markedly the nitric oxide conversion (associated with the number of active sites), but not the temperature threshold of the SCR reaction (associated with the intrinsic reactivity of the active sites). The lower number of active sites on alkali-doped catalyst can be related to the poisoning of both Brønsted and Lewis vanadium acid sites due to alkali addition, which results in a lower ammonia surface coverage.

Ozkan et al. (1993) studied SCR of nitric oxide with ammonia over vanadium pentoxide catalysts with preferential exposure of different crystal planes. Results

from the blank reactor experimental performed at the beginning of the kinetic studies showed no measurable contribution from homogeneous reaction or reactor wall activity. The fact that the catalysts showed essentially no porosity and that they were used in the reactor without pelletizing allowed them to rule out any diffusion limitations. Therefore, the results indicated that vanadium pentoxide catalysts which exhibited preferred exposure of different crystal planes showed marked differences in their catalytic performance in SCR reactions. While characterization results showed that the major difference between these catalysts was the relative abundance of V=O sites. The kinetic studies indicated that the ammonia adsorption took place on at least two different sites located on the basal and side planes. The differences found in the product distribution were explained by considering a complex network of reactions which involved both V=O sites and V-O-V sites and which included both selective reduction of nitric oxide and direct oxidation of ammonia. Another interesting feature of the results was that the increase in the total flow-rate did not seem to affect the product distribution and trends for relative rates of conversion of nitric oxide and ammonia significantly, indicating no significant mass transfer limitations.

Reddy *et al.* (1993) explored effect of thermal treatment on TiO_2-SiO_2 support and V_2O_5/TiO_2-SiO_2 catalysts (1-30 wt.% V_2O_5). The results of V_2O_5/TiO_2-SiO_2 catalysts calcined at $500^{\circ}C$ suggested that vanadia (up to 20 wt.%) was in highly dispersed state on the carrier as an amorphous phase. Thermal treatments at $600^{\circ}C$ and above transformed vanadia and titania into crystalline phases and then TiO_2 anatase into rutile. Without and with $\leq$ 1 wt.% vanadia, the TiO_2-SiO_2 support was thermally quite stable up to $800^{\circ}C$.

Weng & Lee (1993) examined catalytic performance and active sites determination of niobium oxide promoted vanadia/titania catalysts for selective catalytic reduction of nitric oxide with ammonia. It was found that the addition of Nb_2O_5 to V_2O_5/TiO_2 catalysts increased both Lewis acid and Brønsted acid sites with the content of Nb_2O_5 on the catalyst due to the increase in BET surface area, in which the Brønsted acid sites were more significant for the SCR reaction. The enhancement of the catalytic activity in the SCR reaction and ammonia oxidation occured in the

lower and higher temperature ranges, respectively. Due to the Nb_2O_5 promoted vanadia/titania catalysts.

Vikulov *et al.* (1994) studied the SCR of nitric oxide with ammonia over Nb_2O_5- promoted V_2O_5/TiO_2 catalyst. For examination, in contrast to previous claims, the addition of niobia to catalysts containing vanadia supported on titania resulted in much enhanced activity for low-temperature SCR of nitric oxide with ammonia only at low vanadia loading. Niobia promoted catalysts could also be demonstrated to show higher selectivities to N_2, especially at high temperature and low vanadia loading. This enhancement of the activity would not be explained only on the basis of the observation that niobia stabilized the surface area of catalyst. Calculations of the activation energy suggested that a different mechanism of the reaction may be at work at low vanadia loadings.

Matralis *et al.* (1995) explored the influence of the MoO_3 content on catalytic performance for the selective catalytic reduction (SCR) of nitric oxide by ammonia in the presence of oxygen, as well as on textural and structure properties. They reported that the coverage of the TiO_2 support by surface polymeric molybdenum species (where molybdenum was octahedrally coordinated) increased with the molybdenum loading. The formation of a layer of these interacting species on top of the titania surface completed in the range 15-20 wt.% MoO_3. The formation of crystallities of bulk MoO_3 started before the completion of this surface layer (at around 10 wt.% MoO_3) and increased progressively as the molybdenum loading increases from 10 to 20 wt.% MoO_3. The SCR activity of the MoO_3/TiO_2 catalysts increased as the MoO_3 content increased to 15 wt.% and then, for a further increase of the molybdenum loading, it slightly decreased. No specific influence of the molybdenum content on the resistance of catalysts towards SO_2. Their results indicated that the octahedrally coordinated polymeric molybdenum surface species were mainly responsible for the exhibited SCR activity of the MoO_3/TiO_2 catalysts.

Blanco *et al.* (1996) studied the effect of the operation time on the performance of a V_2O_5-WO_3/TiO_2 monolithic catalyst in the reduction of nitrogen

oxide with ammonia. Their studies have shown that the catalytic activity, physical and mechanical properties of the catalyst remained largely unchanged after 5,000 hours of operation even though fly ash and ammonium sulphates were deposited on the exposed catalyst surface. These results clearly demonstrated the high potential for this monolithic catalyst to be used commercially for the control of NO_x emissions from power plants.

Ciambelli *et al.* (1996) identified the influence of sulphate on the catalytic properties of V_2O_5/TiO_2 and WO_3/TiO_2 in the selective reduction of nitric oxide with ammonia. The results indicated that the presence of sulphate should result in increased acidity and then increased activity without reduction of selectivity to nitrogen.

Jehng *et al.* (1996) investigated the effect of water vapor on the molecular structures of V_2O_5- supported catalysts (SiO_2, Al_2O_3, TiO_2 and CeO_2) by in situ Raman spectroscopy as a function of temperature (from 120 to $500^{\circ}C$). Under dry conditions, only isolated surface VO_4 species were present on the dehydrated SiO_2 surface, and multiple surface vanadium oxide species (isolated VO_4 species and polymeric vanadate species) were present on the dehydrated Al_2O_3, TiO_2 and CeO_2 surface. The Raman features of the surface vanadium oxide species on the SiO_2 support were not affected by the introduction of water vapor. This indicated that the molecular structure of the surface vanadium oxide species on SiO_2 was not affected by the presence of water vapor due to the hydrophobic nature of the SiO_2 (Cab-O-Sil) support. However, the presence of water had a pronounced effect on the molecular structures of the surface vanadium oxide species on the Al_2O_3, TiO_2 and CeO_2 supports. The Raman band of the terminal V=O on this oxide supports shifted to lower wavenumbers by 5-30 cm^{-1} and became broad compared to that under dry conditions. Above $230^{\circ}C$, the Raman shift of the surface vanadium oxide species in the presence of water suggested that the dehydrated surface VO_x species formed a hydrogen bond with some adsorbed moisture. The hydrogen-bonded surface VO_x species were extensively solvated by water molecules and formed a hydrated surface vanadate structure upon further decreasing the temperature below $230^{\circ}C$ (*e.g.*,

decavanadate). The Raman band in the 800-900 cm^{-1} region, which is characteristic of the polymerized V-O-V functionality, appeared to be little influenced by the presence of this Raman band. Oxygen-18 isotopic labeling studies revealed that both the terminal V=O and polymeric V-O-V bonds readily underwent oxygen exchange with moisture. The current observations accounted for the inhibiting effect of moisture upon oxidation reactions over supported vanadia catalysts.

Kijlstra et al. (1996) reported the effect of SO$_2$ on the activity for the selective catalytic reduction (SCR) of nitric oxide with ammonia over V$_2$O$_5$/TiO$_2$ catalysts, both unpromoted and promoted by Nb$_2$O$_5$ at temperatures below 200°C. In literature, results were showed that at temperatures below 200°C, the surface of V$_2$O$_5$/TiO$_2$ catalysts could be sulphated by SO$_2$, leading to enhanced Brønsted acidity and to a higher SCR activity. On the other hand, SO$_2$ oxidation followed by (NH$_4$)$_2$SO$_4$ deposition led to deactivation of the catalysts. At low V$_2$O$_5$ loading the former effect dominated, whereas at higher loading deactivation by ammonia sulphates overruled promotion. Doping with Nb$_2$O$_5$ did not suppress SO$_2$ oxidation. At low V$_2$O$_5$ loading, Nb$_2$O$_5$ covered the exposed TiO$_2$ surface, partly blocking the formation of (TiO)$_3$S=O. On a crystalline support Nb$_2$O$_5$ may promote both SCR activity and SO$_2$ oxidation, whereas it did not exert and effect on an amorphous support. The use of a low loaded V$_2$O$_5$ catalyst on a crystalline support without Nb$_2$O$_5$, exhibiting a modest SCR activity after preparation, was advantageous if a stable SCR activity in SO$_2$-containing the gases below 227°C was desired.

Lietti et al. (1996b) investigated the reactivity of V$_2$O$_5$-WO$_3$/TiO$_2$ model catalysts in the reduction of NO by ammonia under steady-state and transient conditions. The results have been compared with those obtained over binary V$_2$O$_5$-WO$_3$/TiO$_2$ samples having the same V$_2$O$_5$ loading. The results indicated that the reactivity of the ternary catalysts in the SCR reaction is higher than that of the vanadia/titania samples. Because the ternary catalysts have the redox properties and surface acidity higher than the binary catalyst. Both the catalyst redox and acid properties were likely playing a role in the SCR reaction over TiO$_2$-supported V$_2$O$_5$-WO$_3$-based catalysts. The redox catalyst functions seemed to govern the catalyst

reactivity in the low temperature region, whereas the occurrence of the SCR reaction in the high temperature region was likely controlled also by the surface acid properties.

Brazdil *et al.* (1997) described a new class of vanadium containing oxide catalysts that were active and selective for the selective catalytic reduction of NO with ammonia. Vanadium antimony oxide based catalysts were found to be effective in the conversion of NO with little or no ammonia slippage. From X-ray diffraction analyses, the catalysts showed that the dominant phase present in the catalyst was vanadium antimonate having a defect rutile crystal structure.

Mongkhonsi *et al.* (1997) exhibited the effects of SO_2 on the SCR activity of V_2O_5/TiO_2 catalysts. The effects were related to the surface structure of V_2O_5. The reactions were tested using simulated exhaust gas in the temperature range 50-500°C. Experimental results revealed that the addition of only a small amount of SO_2 could significantly but not completely deactivate the V_2O_5/TiO_2 catalyst. The deactivation experiment suggested that the V_2O_5/TiO_2 catalyst was deactivated by two mechanisms. The first mechanism was the irreversible adsorption of SO_2 at low temperature. This deactivation mode may be able to be eliminated by raising regeneration temperature. The monolayer structure of V_2O_5 on TiO_2 seemed to be very sensitive to this mode of deactivation. The second deactivation mechanism was the equilibrium adsorption of SO_2. Crystalline V_2O_5 shows higher SO_2 tolerance than the monolayer structure.

Lietti *et al.* (1997) studied the unsteady-state kinetics of NH_3 adsorption-desorption and the SCR of NO_x with NH_3 over V_2O_5/TiO_2 and $V_2O_5-WO_3/TiO_2$ catalysts by transient response techniques. Their results showed that over both catalysts the dynamic experiments could be succesfully described by a kinetic model assuming (1) negligible NO adsorption on the catalyst surface; (2) nonactivated NH_3 adsorption; (3) a Temkin-type NH_3 coverage dependence of the desorption energy; (4) a nonlinear dependence of the SCR reaction rate on the NH_3 surface coverage. Thus, the results were supportive of an Eley-Rideal mechanism for the SCR reaction and of

a significant heterogeneity for adsorption-desorption process and surface reaction of the catalyst surface. Moreover, the binary and ternary catalysts exhibited similar acid properties but different activity in the SCR reaction. Possibly, related to the superior redox properties of the WO_3-containing sample.

Centeno *et al.* (1998) reported an in situ DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) study of NO reduction with NH_3 in the presence of oxygen over lanthanide-doped V_2O_5/Al_2O_3 catalysts. In lanthanide-doped vanadia/alumina catalysts, there seemed to exist a direct relationship between the activity of the catalyst in the SCR reaction and the Brønsted acidity. The addition of lanthanide ions to vanadia/alumian, oxygen and lanthanide ions involved in the V-O-Ln bonds hence changing the acid-base nature of the catalysts. Lewis acidity is enhanced with respect to the undoped catalyst thus leading to an activity decrease. The low activity of the catalysts at low temperature was the results of the adsorption of gaseous NO as nitrate species and the increasing of the fraction of ammonia species adsorbed as coordinated NH_3 over Lewis acid sites, instead of the adsorption as NH_4^+ groups over Brønsted acid sites.

Economidis *et al.* (1998) demonstrated the catalytic performance of $Al_2O_3/SiO_2/TiO_2$ loaded with vanadia for the SCR of NO_x with ammonia. They found that the incorporation of Si and Al as dopants in the support and BET surface area of the catalyst play an important role in the catalyst performance. The coexistence of Al and Si as heteroatoms in the titania matrix resulted in lower levels of activity than titania catalysts due to the low crystallinity of titania in the polyoxide supports. The performance of the catalyst was strongly related with their BET surface area. The Brønsted acidity of the support, which is introduced by the addition of Si and the Al dopants, seem to play a secondary role in the catalyst performance. On the other hand, the addition of Si and Al as heteroatoms decreased the temperature window for optimum performance.

Kamata *et al.* (1998) examined the influence of phosphorus on a commercial V_2O_5-WO_3/TiO_2 of SCR catalyst. In brief, the number of the hydroxyl groups bonded

to the vanadium and titanium species decreased readily with increasing amount of phosphorus. Correspondingly, the hydroxyl groups bonded to the phosphorus species were formed. NH_3 adsorbed on both hydroxyl groups bonded to vanadium and phosphorus as ammonium ions, implying that the P-OH groups formed were also responsible for the Brønsted acidity. The NO reduction activity was found to be decreased with increasing amount of phosphorus. Accordingly the acid strength of the P-OH groups might be weaker than V-OH groups. Plus, phosphorus species might partially wrap the surface V=O and W=O groups, which might also contribute to the deactivation.

Kanongchaiyot *et al.* (1998) demonstrated the effect of loading sequence during the preparation of a W promoted V_2O_5/TiO_2 catalyst (25 %wt. V_2O_5, 5 %wt. WO_3) for the SCR of NO by NH_3 in the presence of oxygen. Tungsten was a second metal oxide added to enhance acidity of the catalyst. The acidity of the catalysts surface were measured using pyridine adsorption technique. It is found that W enhanced both Brønsted acidity and Lewis acidity of the catalysts. The sequence of W loading had some effects on the catalytic activity of the catalyst. Also, loading sequence could change surface acidity of the catalysts.

Koebel & Elsener (1998) measured the kinetic and thermodynamic parameters for three commercial catalysts based on TiO_2-WO_3-V_2O_5 at temperature from 200 to $450°C$ in the presence of water and oxygen. At low temperature, the first-order rate constants strongly depended on NO concentration; this effect decreases with increasing temperature. Therefore, a first-order law with respect to NO could only approximately describe the kinetic behavior of SCR catalysts. A much better description was possible by taking into consideration the adsorption of both NH_3 and NO. However, the relevant parameters were experimentally not accessible with a satisfactory degree of accuracy. At temperature above $350°C$, the thermodynamics of adsorption of SCR-active NH_3 could be studied under realistic SCR-conditions. NH_3, reactive in SCR, is strongly adsorbed and NO is weakly adsorbed. Due to this, the temperature dependence of the respective adsorption constant was strong for NH_3 but

weak for NO. The observed adsorption of NO called either for a reaction mechanism of the Langmuir-Hinshelwood or of the nitrosamidic intermediate.

Nova *et al.* (1998) studied the reactivity in the SCR of TiO_2- supported MoO_3 based catalysts, and compared with that of WO_3/TiO_2 reference catalysts. They reported that the reactivity of the MoO_3/TiO_2 catalysts increased with increasing the MoO_3 loading, whereas the N_2 selectivity decreased due to the formation of undesired N_2O. The formation of N_2O was primarily ascribed to a reaction between NH_3 and NO, and not to the ammonia oxidation reaction. The comparison of the MoO_3/TiO_2 with the WO_3/TiO_2 catalysts having similar molar composition indicated that the WO_3- and MoO_3- containing samples exhibited similar structural and morphological characteristics, but different reactivity: the WO_3/TiO_2 sample was less active but more selective in the SCR reaction. Possibly, the different catalytic behavior has been tentatively ascribed to the different redox characteristics of the samples.

Sintarako *et al.* (1998) discussed the surface acidity of 25 %wt. V_2O_5/TiO_2 catalysts before and after the SCR reaction in both presence and absence of SO_2. Surface acidity of the catalysts before and after the SCR reaction was measured using pyridine adsorption technique. The results suggested that Brønsted acidity rather than Lewis acidity involves in the selective reduction path of NO_x by NH_3. For the catalytic activity test, the presence of SO_2 in a feed composition seems to promote the SCR reaction at the reaction temperature below $300°C$. As for higher temperature, the NO conversion in this region dropped rapidly, indicating severe oxidation of NH_3 to nitrogen oxide especially when SO_2 was present.

Yang *et al.* (1998) investigated the chemisorption of NO in the presence of oxygen on surface TiO_2 which presence and absence sulfate. The unsulphated TiO_2 showed only (strong) Lewis acidity, with no Brønsted acidity. Bidendate SO_4^{2-} ions were formed on TiO_2 upon sulfation, which also generated Brønsted acidity. Morever, on the surface, there was more Brønsted acidity than Lewis acidity (by NH_3 adsorption) at room temperature, which was reserved as the temperature increased. The adsorbed NO (in the presence of O_2) was predominantly in the form of bidendate

NO_3^- ions bonded to Ti sites. In addition, having shift of NO_3^- band on the sulfated TiO_2. Possibly by electron transfer through the S-O-Ti bridge to the neighboring Ti sites, and consequently weakened the adsorption of NO_3^- on the Ti sites.

2.2 The comments on previous papers

From the reviewed literatures, most works use tungsten added on V_2O_5/TiO_2 for promoting the SCR reaction more than other substances (*e.g.* molybdenum, niobium, iron). [Alemany *et al.* (1995), Ciambelli *et al.* (1996), Lietti *et al.* (1996a, b, c), Lietti *et al.* (1997), Dunn *et al.* (1998), Kamata *et al.* (1998)] In their works, catalysts with high loaded of WO_3 (about 10 wt.%) on low loaded of V_2O_5 (about monolayer) are studied. These catalysts show very high TOF in the SCR reaction unlike our catalysts. Moreover, the method of preparation the catalyst is not clear. We do not know that co-loading or sequence loading is the appropriate method. Because some works use co-loading method but other works use sequence loading.

Regarding the catalysts that added potassium, these catalysts are not further studied. In literature reviews, there are a few works studied in low-loaded of both vanadium (about monolayer) and potassium (about 1 wt.%). One review could not clear in effect of potassium. [Shikada & Fujimoto (1983)] And another review told us that potassium had effect on decreasing the acidity of the catalyst. [Lietti *et al.* (1993)] When compared the relative amount of potassium and vanadium that loaded on TiO_2, the percentage of potassium has the value of more than 10 %. [Lietti *et al.* (1993)] Unlike our study, the study is focusol on low-loaded of potassium added on V_2O_5/TiO_2 catalyst.

In many previous literatures, nobody has ever investigated the effect of both tungsten and potassium that added on V_2O_5/TiO_2 catalyst. We think that this is the interesting point for studying.